

Fluctuation symmetries for work and heat

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We consider a particle dragged through a medium at constant temperature as described by a Langevin equation with a time-dependent potential. The time-dependence is specified by an external protocol. We give conditions on potential and protocol under which the dissipative work satisfies an exact symmetry in its fluctuations for all times. We also present counter examples to that exact fluctuation symmetry when our conditions are not satisfied. Finally, we consider the dissipated heat which differs from the work by a temporal boundary term. We explain why there is a correction to the standard fluctuation theorem due to the unboundedness of that temporal boundary. However, the corrected fluctuation symmetry has again a general validity.

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I. INTRODUCTION

Recent years have seen an explosion of results and discussions on a particular symmetry in the fluctuations of various dissipation functions. While started in the context of smooth dynamical systems and of thermostating algorithms and simulations [1, 2], soon the symmetry was judged relevant in the construction of nonequilibrium statistical mechanics. Moreover, a unifying scheme was developed under which the various fluctuation symmetries were found to be the result of a common feature. The basic idea is there that a dissipation function for a physical model can be identified with the source of time-symmetry breaking in the statistical distribution of system histories, see e.g. [3, 4] for more details. That dissipation function is mostly related to the variable entropy production but, depending on the particular realization, can also refer to heat dissipation or to dissipative work. For a given effective model, one of course always needs to check again that basic relation between time-reversal and dissipation.

In the present paper, we look at a particle's position x_t that undergoes a Langevin evolution for a time-dependent potential U_t . Because of that time-dependence, which is externally monitored, work W is done on the particle. At the same time, some of it flows as heat Q to the surrounding medium, checking the conservation of energy $\Delta U = U_\tau(x_\tau) - U_0(x_0) = W - Q$ for the evolution during a time interval $0 \leq t \leq \tau$. Both W and Q are fluctuating quantities and they are path-dependent. Our main result concerns a symmetry in the fluctuations of W . We give conditions on the potential and on its time-dependence U_t under which the fluctuation symmetry for W is exact, i.e., that for all times τ , without further approximation,

$$\frac{\text{Prob}_{\rho_0}(W^{dis} = w)}{\text{Prob}_{\rho_0}(W^{dis} = -w)} = \exp(\beta w) \quad (1)$$

Here, the particle's position is initially distributed with

$\rho_0 \sim \exp(-\beta U_0)$ according to thermal equilibrium at inverse temperature β . The notation W^{dis} refers to the dissipated work (10) which equals the work W up to a difference in free energies. If the evolution would be reversible, then $W^{dis} = 0$. In general, and confirming the second law, we have $\langle W^{dis} \rangle \geq 0$ but (1) also takes into account the trajectories where $W^{dis} < 0$. The exact fluctuation symmetry (1) tells us that such “negative dissipative work” trajectories are exponentially damped.

Since the heat Q differs from the dissipated work only by a temporal boundary term Δ , $Q = W^{dis} - \Delta$ where $\Delta = \Delta(\tau; x_0, x_\tau)$ is non-extensive in time τ , one could perhaps expect that Q satisfies the standard fluctuation symmetry, i.e., that the same as in (1) is true after taking the logarithm and letting $\tau \uparrow +\infty$:

$$\lim_{\tau \uparrow +\infty} \frac{1}{\tau} \log \frac{\text{Prob}_{\rho_0}(Q = q\tau)}{\text{Prob}_{\rho_0}(Q = -q\tau)} \stackrel{?}{=} \beta q \quad (2)$$

for q the heat per unit time. Interestingly, that is not what always happens, see [5]. We will explain how the unboundedness of the potential U_τ can change the symmetry (2). For small enough q (basically, for $0 \leq q\tau \leq \langle W^{dis} \rangle$) the relation (2) remains intact but for all large enough q the lefthand-side of (2) saturates and is constant.

In what follows, we discuss the symmetry relations (1) and (2) in mathematical detail. In particular, we give near to optimal conditions on potential and protocol for which (1) holds. Before, that was shown only for the case of a harmonic potential where the minimum of the potential is moved with a fixed speed via an explicit calculation [5]. There it was also found that (2) can be broken and the modification was explicitly calculated. Here we will argue for more general protocols and potentials to give estimates about the range of validity of (2). The main point is to understand when and how terms, non-extensive in the time τ , can still contribute to the large deviations of the heat Q .

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II. MODEL AND RESULTS

In the present paper we apply the general scheme and algorithm of [3, 4] to a model that has previously and recently been considered by a number of groups [5, 6, 7, 8]. We find optimal conditions on potential and protocol under which the dissipated work satisfies an exact fluctuation symmetry, i.e., one that is valid for all times. The heat differs from that dissipated work via a temporal boundary term and also satisfies some general fluctuation symmetry asymptotically in time. Because the potential is unbounded, that last symmetry is not the same as in the standard steady state fluctuation theorem. Below we give more details.

A. Model

We consider a family of one-dimensional potentials $U_t, t \in [0, \tau]$, as parameterized via a deterministic protocol γ_t : $U_t(x) = U(x, \gamma_t)$, with $x, \gamma_t \in \mathbb{R}$. The corresponding equilibria at inverse temperature β are

$$\rho_t(x) \equiv \frac{e^{-\beta U_t(x)}}{Z_t} \quad (3)$$

$$Z_t \equiv \exp[-\beta F_t] \equiv \int_{-\infty}^{+\infty} dx e^{-\beta U_t(x)}$$

with Helmholtz free energy F_t . The time-dependence in γ_t is supposed to be given and can be quite arbitrary; of course the partition function Z_t must be finite. The dynamics is now specified by a Langevin-Itô-type equation

$$dx_t = -\frac{\partial U_t}{\partial x}(x_t) dt + \sqrt{\frac{2}{\beta}} db_t \quad (4)$$

where db_t is standard white noise. Such dynamics have been considered before in a wide variety of contexts but for fluctuation theorems the emphasis has been on the Gaussian case. An experimental realization [8] of that dynamics was theoretically investigated by [5], who started from (4) with

$$U_t(x) = \frac{(x - vt)^2}{2} \quad (5)$$

A more general analysis for driven harmonic diffusive systems was given in [9]. Quite recently in [6] further experiments were considered for more general potentials and protocols.

In the present paper we work with the general (3) but we sometimes restrict ourselves to the physically relevant case of

$$U_t(x) = U(x - \gamma_t) \quad (6)$$

for a given protocol $\gamma = (\gamma_t, t \in [0, \tau])$ that marks the shift in a potential U as time goes on. In that case F_t

does not depend on time and the associated difference in free energies

$$\Delta F = -\frac{1}{\beta} \ln \left(\frac{Z_\tau}{Z_0} \right) \quad (7)$$

is zero.

The model (4) defines a Markov diffusion process. We write

$$\omega = (x_t, t \in [0, \tau])$$

for the (random) positions of the particle. If the initial distribution of the position x_0 is given via a density ρ , then $\text{Prob}_\rho(\omega|\gamma)$ denotes the probability density of observing a trajectory ω under the influence of the protocol γ , with respect to the thermal noise $\sqrt{2/\beta} db_t$. Given a path ω and a protocol γ we also consider their time-reversed versions:

$$\begin{aligned} \Theta \omega_i &\equiv \omega_{\tau-i} = x_{\tau-i} \\ \Theta \gamma_i &\equiv \gamma_{\tau-i} \end{aligned} \quad (8)$$

B. Problem

The observables of interest are the work and the heat.

The work W_γ is associated to the external agent, in changing the potential via the protocol γ ,

$$W_\gamma(\omega) \equiv \int_0^\tau dt \dot{\gamma}_t \frac{\partial U_t}{\partial \gamma_t}(x_t) \quad (9)$$

The dissipative work can then be identified with

$$W_\gamma^{dis}(\omega) = W_\gamma(\omega) - \Delta F \quad (10)$$

One has to remember here that for a reversible and isothermal evolution the change in free energy precisely equals the work W_γ done on the system. Furthermore, in the situation (6) one has $\Delta F = 0$ so that $W_\gamma = W_\gamma^{dis}$.

The heat Q_γ is most easily defined via the first law of thermodynamics.

$$\Delta U = U_\tau(x_\tau) - U_0(x_0) = W_\gamma(\omega) - Q_\gamma(\omega)$$

$$Q_\gamma(\omega) \equiv - \int_0^\tau dx_t \circ \frac{\partial U_t}{\partial x}(x_t) = - \int_0^\tau dt \dot{x}_t \frac{\partial U_t}{\partial x}(x_t) \quad (11)$$

The integral (with the “ \circ ”) should be understood in the sense of Stratonovich; it coincides better with the usual intuition of integrals and it does not suffer from the lack of time-symmetry in the Itô integral which will be important for us, see also [10].

In the present paper we ask

1. under what conditions the work (9) or (10) satisfies an exact fluctuation symmetry (EFS) (1).
2. what are the possible corrections to the standard fluctuation symmetry (2) for the fluctuations of the heat (11).

So far, these questions have been theoretically investigated via explicit computation for the special case of a linearly dragged particle in the harmonic potential (5), in [5]; question (2) has been generally addressed in [11]. Experimental and numerical work (in agreement with the results below) was done in [6, 7, 8, 12].

C. Results

We start with the exact fluctuation symmetry for the work (9). First we consider the harmonic case $U(x) = x^2/2$ with a general protocol γ_t as in (6). Then we give a general condition under which the work satisfies an EFS, and we give instances under which that condition is satisfied. Counter examples (for which the work does not satisfy an EFS) will show why these conditions are close to optimal. We end with a discussion on the relevance of temporal boundary terms in the large deviations of the heat (11). For the proofs we refer to section IV.

1. Work

First look at quadratic potentials, e.g. for

$$U_t(x) = \frac{(x - \gamma_t)^2}{2} \quad (12)$$

which coincides with the potential (5) if $\gamma_t = vt$. For that class of quadratic potentials, as in (12), one has a Gaussian distribution of the work (9) for all protocols γ_t .

In what follows the probability density for the (dissipated) work is denoted by $\text{Prob}_{\rho_0}(W_\gamma^{(dis)}(\omega) = w)$ as a function of $w \in \mathbb{R}$. This (dissipated) work $W_\gamma^{(dis)}$ depends on the time τ , see (9) - (10).

Proposition II.1 (Harmonic case).

If the distribution of the work W_γ is Gaussian, then for a general protocol γ_t in (6):

$$\frac{\text{Prob}_{\rho_0}(W_\gamma^{dis}(\omega) = w)}{\text{Prob}_{\rho_0}(W_\gamma^{dis}(\omega) = -w)} = \exp(\beta w) \quad (13)$$

for all times τ .

That fluctuation symmetry is easily checked to hold also for quadratic potentials which are more general than (12). One could argue that any Gaussian distributed observable can be made to satisfy a fluctuation theorem

by rescaling the mean and the variance. However, that is not what happens here: no scaling at all is required for the work W_γ to satisfy the exact fluctuation symmetry.

For more general potentials, we start by specifying a general condition:

Assumption: We assume that there exists an involution s on path-space, $s^2 = \mathbb{1}$, with $s\Theta = \Theta s$ and such that

$$\text{Prob}_{\rho_\tau}(\omega|\Theta\gamma) = \text{Prob}_{\rho_0}(s\omega|\gamma) \quad (14)$$

The involution s relates trajectories under the protocol γ and its time-reversed protocol $\Theta\gamma$. The next theorem stipulates that the existence of s implies an exact fluctuation theorem for the work. We illustrate that assumption below by enumerating the cases where the assumption is certainly verified, see also in Section III.

Theorem II.2 (EFS Work).

Under the assumption (14) above, the dissipative work (10) satisfies an EFS: for all $\tau > 0$ and for all w ,

$$\frac{\text{Prob}_{\rho_0}(W_\gamma^{dis}(\omega) = w)}{\text{Prob}_{\rho_0}(W_\gamma^{dis}(\omega) = -w)} = \exp(\beta w) \quad (15)$$

The assumption (14) can be split in some two subassumptions as we now state.

Proposition II.3.

Suppose either (i) that the protocol is symmetric under time-reversal $\gamma_t = \gamma_{\tau-t} \equiv \Theta\gamma_t$, or (ii) that the protocol is antisymmetric $\gamma_t - \gamma_0 = \gamma_\tau - \gamma_{\tau-t} \equiv -\Theta(\gamma_t - \gamma_0)$ and that the potential U obeys (6) and is symmetric, $U(x) = U(-x)$. Then assumption (14) and hence the EFS (15) are verified.

The EFS for the harmonic case $U(x) = x^2/2$ with constant velocity $\gamma_t = vt$ as in (5), see [5, 8], is treated by Proposition II.1 but is of course also a special case of Proposition II.3.

We will see further in Section III A how our conditions are in fact optimal. We can however already observe here how some symmetry of the protocol must enter when dealing with an arbitrary potential. Consider indeed, if only formally, $U(x) = x, x > 0$ with a wall $U(x) = +\infty$ for $x \leq 0$ in (9). We can then safely assume that the trajectory satisfies $x_t - \gamma_t > 0$ and (9) gives that the work $W_\gamma = W_\gamma^{dis} = \gamma_\tau - \gamma_0$. Obviously this (constant) expression never satisfies an EFS unless (and then trivially) $\gamma_\tau = \gamma_0$.

2. Heat

The heat Q_γ defined in (11) equals the dissipative work W_γ^{dis} up to some temporal boundary term:

$$Q_\gamma = W_\gamma^{dis} + \Delta(F - U)$$

The temporal boundary $\Delta(F - U)$ is, modulo the factor β , the change of equilibrium entropy in going from the equilibrium described by ρ_0 to that given by ρ_τ . For the fluctuations of the heat we start from a situation where we already have the EFS (15) for the (dissipative) work.

We are here concerned with the situation where the potential in (6) is unbounded and we assume that for some $\varepsilon, v > 0$

$$U(x) \geq |x|^{1+\varepsilon}, \gamma_t = vt \quad (16)$$

at least for $|x|$ and t sufficiently large. For the average work we write

$$\lim_{\tau \rightarrow +\infty} \frac{\langle Q_\gamma \rangle}{\tau} = \lim_{\tau \rightarrow +\infty} \frac{\langle W_\gamma \rangle}{\tau} \equiv \bar{w}$$

We further continue to assume the well-defined dynamics (4) with the EFS (15) for the (dissipative) work. The latter can be summarized by introducing the rate function $I(w)$ which, in logarithmic sense and asymptotically as $\tau \uparrow +\infty$, governs

$$\text{Prob}(W_\gamma^{dis} = w\tau) = \exp[-\tau I(w)]$$

and assuming that $I(w) \geq 0$ is strictly convex with minimum at \bar{w} , $I(\bar{w}) = 0$ and which, from the EFS (15), satisfies $I(-w) - I(w) = \beta w$. Let w^* be the solution of $I'(w) = \beta$. In case the rate function $I(w)$ is symmetric around $w = \bar{w}$, then $w^* = 3\bar{w}$.

Under these assumptions, we will argue in Section IV D that the following holds true in general:

Consider, as in (2), for $q \geq 0$,

$$f(q) \equiv \lim_{\tau \rightarrow +\infty} \frac{1}{\tau} \log \frac{\text{Prob}(Q_\gamma = \tau q)}{\text{Prob}(Q_\gamma = -\tau q)} \quad (17)$$

Then,

$$f(q) = \begin{cases} \beta q & \text{for } 0 \leq q \leq \bar{w} \\ \beta q - I(q) & \text{for } \bar{w} \leq q \leq w^* \\ \beta w^* - I(w^*) & \text{for } q \geq w^* \end{cases}$$

The antisymmetry of $f(q) = -f(-q)$ fixes the behavior for $q < 0$.

As an example, take $I(w) = \beta(w - \bar{w})^2/4\bar{w}$ as is the case for (5), see [5]. Then $w^* = 3\bar{w}$ and we have three regimes. A first linear regime where we see the usual symmetry (15) for $0 < q \leq \bar{w}$, then a quadratic regime for $\bar{w} < q \leq 3\bar{w}$ which saturates to a fixed value for $q \geq 3\bar{w}$. Under our assumptions, we have now a general expression for the symmetry of the heat fluctuations, extending the results in [5] quite beyond the harmonic case (5).

A more probabilistic interpretation and a toy-calculation is presented in Appendix II.

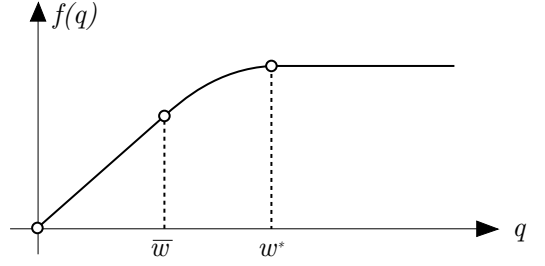


FIG. 1: Deviations from the fluctuation symmetry (2) for the heat per unit time q . The function $f(q)$ is defined in (17). For small values of q , $f(q)$ is linear so the standard fluctuation theorem is recovered. Between \bar{w} and w^* , the behavior is determined by the large deviation rate-function $I(q)$ of the work. The function $f(q)$ saturates for large q .

III. EXPERIMENTS AND NUMERICAL WORK

A. Simulations

In the previous sections, we have given conditions on the protocol and on the potential for the work to follow an EFS (15). We now argue via numerical examples that our sufficient conditions are also close to being necessary. To that aim, we have simulated the Langevin motion of the particle by means of an Euler-Maruyama scheme. The time interval $[0, \tau]$ is divided into n parts $dt = \tau/n$, and the evolution of the system takes place via discrete states x_i ($i = 0, 1, 2, \dots, n$) connected by finite dt steps,

$$x_{i+1} = x_i - \frac{\partial U(x_i, \gamma_i)}{\partial x} dt + \sqrt{2dt} B_i$$

where B_i is a random number drawn from a normal distribution, and we have set $\beta = 1$. The work (9) is calculated through

$$W = - \sum_{i=0}^{n-1} U'(x_i - \gamma_i)(\gamma_{i+1} - \gamma_i)$$

We consider the asymmetric potential, for $\alpha_+, \alpha_- > 0$,

$$U_t(x) = U(x - \gamma_t) = \begin{cases} \frac{|x - \gamma_t|^{\alpha_+}}{\alpha_+} & \text{for } x \geq \gamma_t \\ \frac{|x - \gamma_t|^{\alpha_-}}{\alpha_-} & \text{for } x < \gamma_t \end{cases} \quad (18)$$

The first case examined is where the potential above is moved with a linear protocol $\gamma_t = t$ for $t > 0$. At $t = 0$, we generate equilibrated configurations, sampled with a usual Markov chain and a Metropolis criterion. First we chose a generic (non-harmonic) symmetric potential, with $\alpha_+ = \alpha_- = 3$, for which we expect the EFS (15) to hold. That is confirmed in figure 2, in which we plot the difference

$$\ln \left[\frac{P(W = w)}{P(W = -w)} \right] - w$$

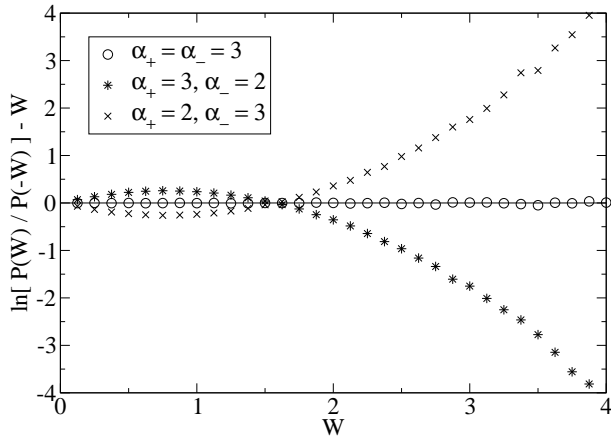


FIG. 2: Plot of the deviations from the EFS (15), for several values of the exponents α_+ and α_- in (18). A potential which is dragged with constant velocity $v = 1$ is considered: the EFS is verified for the symmetric potential (here we chose $\alpha_+ = \alpha_- = 3$), while it is not observed for asymmetric potentials. Parameters are $\tau = 1$ and $dt = 10^{-3}$.

between the lefthand-side and the righthand-side in (15). Indeed, there are no noticeable deviations from zero for the case of a symmetric potential. On the other hand, in the same figure, the results found for asymmetric potentials are not in agreement with the EFS. In that case the conditions of Proposition II.3 are not verified. Note that the symmetric deviations from the origin found for the choices $(\alpha_+ = 3, \alpha_- = 2)$ and $(\alpha_+ = 2, \alpha_- = 3)$ represent an indirect verification of the Crooks relation, see further in Section IV A.

In figure 3, one sees again how our conditions in Proposition II.3 are necessary. This time we take a protocol that lacks the suitable temporal symmetries, like $\gamma_t = t + t^4$. The EFS is then not verified even for a symmetric potential as in (18) with $\alpha_+ = \alpha_- (\neq 2)$. However, as expected, the simulation of the special case of the harmonic potential $\alpha_+ = \alpha_- = 2$ obeys the conclusion of Proposition II.1. Similar conclusions are drawn from figure 4.

B. Experiments

Previous experiments to test the fluctuation theorem for nonequilibrium systems included a particle dragged in water. In [8], Wang *et al.* consider a particle equilibrated in an optical trap and then dragged by the trap at constant speed relative to the surrounding water. The particle is micron-sized, the force is of order of pico-Newton and about 500 particle trajectories were recorded for times up to 2 seconds after initiation. The protocol specifies the time-dependent position of the trap, approximated as the position of the minimum in a harmonic potential with spring constant κ . The external force exerted on the particle is thus $F_t(q) = -\kappa(q - \gamma_t)$.

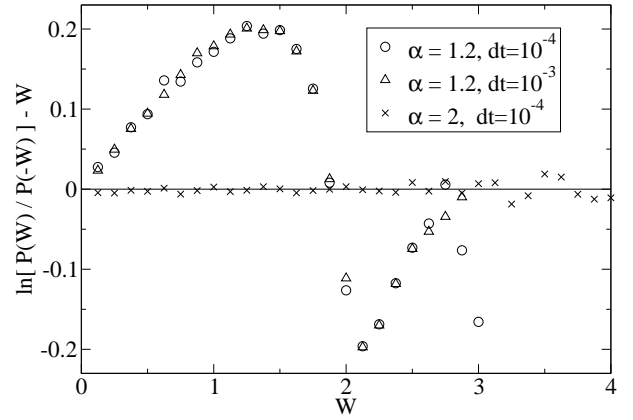


FIG. 3: Plot of the deviations from the EFS (15), for symmetric potentials [$\alpha_+ = \alpha_- \equiv \alpha$ in (18)] and spatially translated with protocol $\gamma_t = t + t^4$. We chose $\tau = 1$ and $dt = 10^{-4}$. The fluctuation theorem is verified for the harmonic potential, while it is not valid for a symmetric potential with exponent $\alpha_+ = \alpha_- = 1.2$. For the latter potential, a simulation with $dt = 10^{-3}$ shows that numerical approximation is negligible.

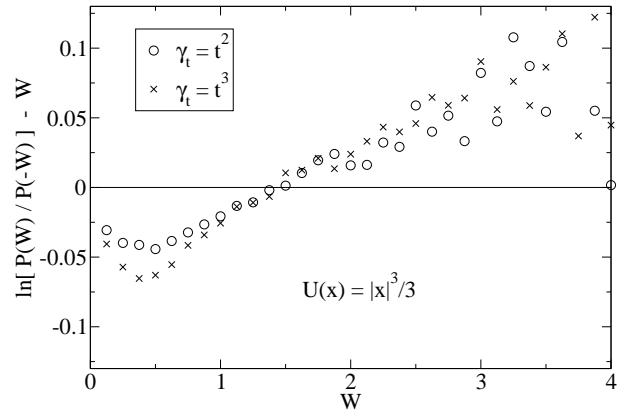


FIG. 4: Plot of the deviations from the EFS (15), for the symmetric potential $U(x) = |x|^3/3$ [$\alpha_+ = \alpha_- = 3$ in (18)] and spatially translated with protocol $\gamma_t = t^2$ and $\gamma_t = t^3$. We chose $\tau = 1$ and $dt = 10^{-4}$. Since both protocols are neither symmetric or antisymmetric, the EFS is indeed not expected to hold.

The motion of $\gamma_t = vt$ is about rectilinear. In a second experiment, [7], the shape of the confining potential was changed. However, both are examples of harmonic potentials, which we have shown to be a very special class.

More recently, more general situations have been investigated, see [6, 12]. E.g. a two level system was realized experimentally with a single defect in a diamond. When the system is externally driven by a laser, the dissipation $R = \beta W^{dis}$ displays non-Gaussian fluctuations. It was noticed that integrated versions of the fluctuation the-

orem in their experiment are observed only for particular protocols, in line with our general results about the symmetric protocols (Proposition II.3). In the more recent paper [6], the distribution of the work performed on a particle was computed for a non-harmonic potential. Again, the time-symmetric protocol has been found to yield results consistent with the EFS. Note however that our results show that a symmetric protocol is not necessary; also the application of an antisymmetric (e.g. linear) protocol combined with a symmetric potential provides a verification of the EFS (see Proposition II.3 and figure 2).

IV. PROOFS

A. Exact identities (Crooks and Jarzynski relations)

The proofs of the results listed in section II C are discussed here. The basic ingredient for approaching the fluctuations of dissipation functions via the method of time-reversal was already mentioned in the introduction. In particular, for stochastic dynamics and especially those that we study here under equation (4), the following relation is known as the Crooks fluctuation theorem, see [13]; remember the notation around (8):

Lemma IV.1.

$$\frac{\text{Prob}_{\rho_0}(\omega|\gamma)}{\text{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)} = \exp(\beta(W_\gamma(\omega) - \Delta F)) \quad (19)$$

Proof. Using the Girsanov formula [14], the probability density $\text{Prob}_{\rho_0}(\omega|\gamma)$ on trajectories can be expressed in terms of the potential. Remember that the reference measure is associated to the $U = 0$ case (pure Brownian trajectories), starting from ρ_0 ,

$$\begin{aligned} & \text{Prob}_{\rho_0}(\omega|\gamma) \\ &= \exp \left[-\frac{\beta}{2} \int_0^\tau dx_t \circ \frac{\partial U_t}{\partial x}(x_t) + ST \right] \\ &= \exp \left[\frac{\beta Q_\gamma(\omega)}{2} + ST \right] \end{aligned} \quad (20)$$

where

$$ST = \frac{\beta}{4} \int_0^\tau dt \left[\frac{\partial^2 U_t}{\partial x^2}(x_t) - \left(\frac{\partial U_t}{\partial x}(x_t) \right)^2 \right]$$

The ratio of time-forward and time-backward probabilities can then be computed by using

$$Q_{\Theta\gamma}(\Theta\omega) = -Q_\gamma(\omega) \quad (21)$$

$$\Theta(ST) = ST$$

That leads to

$$\begin{aligned} \frac{\text{Prob}_{\rho_0}(\omega|\gamma)}{\text{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)} &= \frac{\rho_0(x_0)}{\rho_\tau(x_\tau)} \exp[\beta Q_\gamma(\omega)] \\ &= \exp[\beta \Delta U - \beta \Delta F + \beta Q_\gamma(\omega)] \end{aligned}$$

which is (19) since $\Delta U = -Q_\gamma + W_\gamma$. \square

From the Crooks relation (19) follows easily the so called Jarzynski relation [15]. In our context, this is the normalisation of the probability distribution,

$$1 = \left\langle \frac{\text{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)}{\text{Prob}_{\rho_0}(\omega|\gamma)} \right\rangle_{\rho_0} = e^{\beta \Delta F} \langle e^{-\beta W_\gamma(\omega)} \rangle_{\rho_0}$$

where $\langle \cdot \rangle_{\rho_0}$ is the expectation starting from ρ_0 . Conclusion:

$$e^{-\beta \Delta F} = \langle e^{-\beta W_\gamma(\omega)} \rangle_{\rho_0} \quad (22)$$

A more microscopic and physically inspired derivation of the Jarzynski relation follows in Appendix I.

B. The harmonic potential with a general protocol

For the harmonic potential (12), all protocols γ lead to an exact fluctuation symmetry for the work. The proof can easily be generalized to other quadratic forms of the potential where for example the protocol works multiplicatively (e.g. $U_t(x) = U(\gamma_t x)$).

From the definition of work (9), it is easy to see that the distribution of the work is Gaussian in the case of a harmonic potential.

Proposition II.1. The free energy difference (7) satisfies $\Delta F = 0$ for all possible protocols γ_t . If the distribution of the work is Gaussian with mean \bar{w} and variance σ^2 , the expectation value in (22) can be computed explicitly:

$$1 = \langle e^{-\beta W_\gamma(\omega)} \rangle = \exp \left[\frac{1}{2\sigma^2} (-2\bar{w}\sigma^2\beta + \sigma^4\beta^2) \right]$$

Thus, necessarily, $\bar{w} = \frac{1}{2}\sigma^2\beta$.

Finally, it is easy to check that a Gaussian random variable whose mean \bar{w} and variance σ^2 are related by $\bar{w} = \frac{1}{2}\sigma^2\beta$ satisfies (13). \square

C. Work EFS

By applying property (14) of the involution s to the numerator and denominator of the Crooks relation (19), we

find:

$$\begin{aligned} \exp [\beta(W_\gamma(\omega) - \Delta F)] &= \frac{\text{Prob}_{\rho_0}(\omega|\gamma)}{\text{Prob}_{\rho_\tau}(\Theta\omega|\Theta\gamma)} \\ &= \frac{\text{Prob}_{\rho_\tau}(s\omega|\Theta\gamma)}{\text{Prob}_{\rho_0}(\Theta s\omega|\gamma)} \\ &= \exp [-\beta(W_\gamma(s\Theta\omega) + \Delta F)] \end{aligned}$$

Hence,

$$W_\gamma(s\Theta\omega) = -W_\gamma(\omega) + 2\Delta F \quad (23)$$

From the first law combined with (21) one also concludes that $W_{\Theta\gamma}(\Theta\omega) = -W_\gamma(\omega)$.

Theorem II.2. Let us explicitly denote the dependence of the dynamics on the protocol γ by writing $\text{Prob}_{\rho_0}(W_\gamma = w|\gamma)$ for the density of the work W_γ . By (19)

$$\begin{aligned} \text{Prob}_{\rho_0}(W_\gamma(\omega) = w'|\gamma) \\ = e^{\beta(w' - \Delta F)} \text{Prob}_{\rho_\tau}(W_\gamma(\Theta\omega) = w'|\Theta\gamma) \end{aligned}$$

By (14):

$$\begin{aligned} \text{Prob}_{\rho_\tau}(W_\gamma(\Theta\omega) = w'|\Theta\gamma) \\ = \text{Prob}_{\rho_0}(W_\gamma(\Theta s\omega) = w'|\gamma) \end{aligned}$$

As a consequence, via (23)

$$\begin{aligned} \text{Prob}_{\rho_0}(W_\gamma(\omega) = w'|\gamma) \\ = e^{\beta(w' - \Delta F)} \text{Prob}_{\rho_0}(W_\gamma(\omega) = 2\Delta F - w'|\gamma) \end{aligned}$$

Substituting $w' = w + \Delta F$, we find the EFS (15) as required. \square

Proposition II.3. Suppose first a symmetric protocol $\Theta\gamma = \gamma$ and hence $\gamma_\tau = \gamma_0$,

$$U_0(x) = U_\tau(x) \quad \Rightarrow \quad \rho_0(x) = \rho_\tau(x)$$

with ρ_t the distribution (3). Choosing the identity operator as the involution $s = \mathbb{1}$, i.e., $s\omega = \omega$, we find that (14) is obviously satisfied.

For antisymmetric protocols $\gamma_{\tau-t} = X - \gamma_t$ with $X = \gamma_0 + \gamma_\tau$ we restrict ourselves to symmetric potentials of the form (6). Observe then that

$$U(X - x - \gamma_t) = U(-x + \gamma_{\tau-t}) = U(x - \gamma_{\tau-t})$$

which, for $t = 0$, implies $\rho_0(X - x) = \rho_\tau(x)$. Choose therefore the involution s in (14) as the flip $s\omega = X - \omega$, in the sense that $s(\omega)_t = X - x_t$ for $\omega = (x_t)$. Then, by simple inspection from (20), again by using that the potential U is even, we get the equality $\text{Prob}_{\rho_0}(s\omega|\gamma) = \text{Prob}_{\rho_\tau}(\omega|\Theta\gamma)$ of densities, as for (14). \square

D. Heat FT

We give the arguments leading to (17). Here we do not give a full proof.

For very large τ it is appropriate for our purpose to consider $Q_\gamma/\tau = W_\gamma^{dis}/\tau + \Delta(F - U)/\tau$ as the sum of two independent random variables. That asymptotic independence can be argued for on the basis of mixing properties of the Markov diffusion process (4). We thus write formally, for arbitrary q ,

$$\begin{aligned} \text{Prob}(Q_\gamma = q\tau) &= \text{Prob}(W_\gamma^{dis} + \Delta(F - U) = q\tau) \\ &= \int dw e^{-\tau[I(w) + J(q-w)]} \end{aligned} \quad (24)$$

where $\text{Prob}(W_\gamma^{dis} = w\tau) = \exp[-\tau I(w)]$, $\text{Prob}(\Delta(F - U) = u\tau) = \exp[-\tau J(u)]$ in the usual sense of the theory of large deviations, as $\tau \uparrow +\infty$.

Hence, taking the logarithm of (24) and dividing by $\tau \uparrow +\infty$ takes us to

$$h(q) \equiv \lim_{\tau \uparrow +\infty} \frac{1}{\tau} \log \text{Prob}(Q_\gamma = q\tau) = -\inf_w [I(w) + J(q-w)] \quad (25)$$

and we want to compute $f(q) = h(q) - h(-q)$. As $I(w)$ is the rate function of the large deviations of the (dissipative) work, which we assume given and satisfying the EFS (15), the only unknown is the rate function J .

Clearly, always in the sense of large deviations,

$$J(u) = -\lim_{\tau \uparrow +\infty} \frac{1}{\tau} \log \text{Prob}_{\rho_0} \left(\frac{U(x_0) - U(x_\tau - v\tau)}{\tau} = u \right)$$

Here we assume again the independence for large τ , this time between the variables $U(x_0)$ and $U(x_\tau - v\tau)$. Since $U_t(x) \geq 0$, if $u > 0$, then, by this independence,

$$J(u) = -\lim_{\tau \uparrow +\infty} \frac{1}{\tau} \log \int_u^{+\infty} dy e^{-\beta y \tau} \text{Prob}_{\rho_0}(U(x_\tau - v\tau) = (y - u)\tau) \simeq \beta u$$

On the other hand, if $u < 0$, we have

$$J(u) = -\lim_{\tau \uparrow +\infty} \frac{1}{\tau} \log \text{Prob}_{\rho_0}(U(x_\tau - v\tau) = -u\tau)$$

Now, the process $x_\tau - v\tau$ is stationary for large τ : from

equation (4)

$$d(x_t - vt) = -U'(x_t - vt) dt - v dt + \sqrt{\frac{2}{\beta}} db_t$$

so that we can expect that for large τ , $x_\tau - v\tau$ is distributed according to the Boltzmann statistics $\exp[-\beta U(x_\tau - v\tau) - \beta v(x_\tau - v\tau)]$. As $U(x) \geq |x|^{1+\varepsilon}$, we have that for $u < 0$, $J(u) = -\beta u$.

Summarizing, in (24) we can take $J(u) = \beta|u|$. After all, it gives the probability of finding a huge energy difference $\Delta(F - U) \simeq u\tau$ between the initial and the final state. It means that either $U_0(x_0)$ or $U_\tau(x_\tau)$ must be very large, and the energy has, in Boltzmann statistics, an exponential distribution.

Finally, to obtain the results from section II C 2 one must still use that

$$-I(w) + I(-w) = \beta w, \quad I'(w) + I'(-w) = -\beta$$

so that e.g. $I'(-\bar{w}) = -\beta$. It is then easily seen that $h(q) = -I(-\bar{w}) + \beta(\bar{w} + q)$ if $q \leq -\bar{w}$, $h(q) = -I(q)$ if $-\bar{w} \leq q \leq w^*$ and $h(q) = -I(w^*) - \beta(q - w^*)$ if $q \geq w^*$. From these one computes $f(q) = h(q) - h(-q)$.

Appendix I: The basis of a Jarzynski relation

Let Γ be the phase space on which we have a time-dependent dynamics [18] defined in terms of invertible transformations f_t . One can think of a protocol γ that changes in discrete steps so that a phase space point $x \in \Gamma$ flows in time t to $\varphi_{t,\gamma}x \in \Gamma$ with

$$\varphi_{t,\gamma} = f_t \dots f_2 f_1, \quad t = 1, \dots, \tau$$

For the reversed protocol $\Theta\gamma$,

$$\varphi_{t,\Theta\gamma} = f_{\tau-t+1} \dots f_{\tau-1} f_\tau$$

We imagine a measure μ on the phase space Γ that is left invariant by $\varphi_{t,\gamma}$: $\mu(\varphi_{t,\gamma}^{-1}B) = \mu(B)$ for $B \subset \Gamma$. Furthermore, Γ is equipped with an involution π that also leaves μ invariant. We assume dynamical reversibility in the sense that for all t ,

$$f_t \pi = \pi f_t^{-1}$$

As a consequence, $\pi \varphi_{t,\Theta\gamma}^{-1} \pi = f_\tau \dots f_{\tau-t+1}$ or $\varphi_{\tau,\gamma}^{-1} \pi \varphi_{t,\Theta\gamma}^{-1} \pi = \varphi_{\tau-t,\gamma}^{-1}$.

Let us now divide the phase space in a finite partition $\hat{\Gamma}$. It corresponds to a reduced description; each element in the partition is thought to reflect some manifest condition of the system. The entropy is defined à la Boltzmann as

$$S(M) = \ln \mu(M), \quad M \in \hat{\Gamma}$$

For example, in Hamiltonian systems one takes the Liouville measure as the invariant measure μ , and then we obtain the conventional Boltzmann definition $S = \ln |M|$. We fix probability laws $\hat{\rho}$ and $\hat{\sigma}$ on the elements of the partition and we specify the initial probability measure on Γ as

$$r_{\hat{\rho}}(A) \equiv \sum_M \frac{\mu(A \cap M)}{\mu(M)} \hat{\rho}(M)$$

This probability measures $A \subset \Gamma$ using $\hat{\rho}$ at the level of the partitions M of the reduced description and using the invariant measure μ within each partition M . The reduced trajectories of the system are sequences $\omega = (M_0, M_1, \dots, M_\tau)$ where $M_i \in \hat{\Gamma}$, indicating subsequent moments when the phase space point was in the set M_i , $i = 0, \dots, \tau$. The path-space measure $P_{\hat{\rho},\gamma}$ gives the probability of trajectories when starting from $r(\hat{\rho})$ and using protocol γ .

The quantity of interest that measures the irreversibility in the dynamics on the level of $\hat{\Gamma}$ is (see also (19) and [4]):

$$R = \ln \frac{P_{\hat{\rho},\gamma}(M_0, M_1, \dots, M_\tau)}{P_{\hat{\sigma},\Theta\gamma}(\pi M_\tau, \pi M_{\tau-1}, \dots, \pi M_0)}$$

The point is that for every probability $\hat{\rho}$ and $\hat{\sigma}$ on $\hat{\Gamma}$, and for all $M_0, \dots, M_\tau \in \hat{\Gamma}$,

$$R = S(M_\tau) - S(M_0) - \ln \hat{\sigma}(M_\tau) + \ln \hat{\rho}(M_0) \quad (26)$$

To show (26) we only have to look closer at the consequences of the dynamic reversibility. By using that $\mu(B) = \mu(\varphi_{\tau,\gamma}^{-1}\pi B)$, we have of course that

$$\mu \left[\bigcap_{t=0}^{\tau} \varphi_{t,\Theta\gamma}^{-1} \pi M_{\tau-t} \right] = \mu \left[\bigcap_{t=0}^{\tau} \varphi_{\tau,\gamma}^{-1} \pi \varphi_{t,\Theta\gamma}^{-1} \pi M_{\tau-t} \right]$$

but moreover, by reversibility, the last expression equals

$$\mu \left[\bigcap_{t=0}^{\tau} \varphi_{\tau,\gamma}^{-1} \pi \circ \varphi_{t,\Theta\gamma}^{-1} \pi M_{\tau-t} \right] = \mu \left[\bigcap_{t=0}^{\tau} \varphi_{\tau-t,\gamma}^{-1} M_{\tau-t} \right]$$

which is all that is needed.

As an immediate corollary, under the expectation $P_{\hat{\rho},\gamma}$

$$\langle e^{-S(M_\tau) + S(M_0) + \ln \hat{\sigma}(M_\tau) - \ln \hat{\rho}(M_0)} \rangle = 1 \quad (27)$$

A simple choice for the system and partition takes an isolated system where the reduced variables M_i refer to the energy of the system. We have still the freedom to choose $\hat{\rho}$ and $\hat{\sigma}$. Let us take $\hat{\rho}(M_0) = 1$ where indeed M_0 refers to the initial energy E . As final condition we let the system be randomly distributed on the energy shell E' . For these choices, in ‘suggestive’ notation, (27) becomes

$$\ln \frac{P_{E,\gamma}(E \rightarrow E')}{P_{E',\Theta\gamma}(E' \rightarrow E)} = S(E') - S(E)$$

Using that here $\Delta E = E' - E = W$ equals the work done, one thus recovers the microcanonical analogue of the Crooks relation (19), see also [16].

The mathematically trivial identity (27) is the mother of all Jarzynski relations. The way in which it gets realized as for example an irreversible work-free energy relation depends on the specific context or example. We can also split the system from the environment. The reduced variables (M_i) can for example be chosen to consist of the microscopic trajectory for the system and of the sequence of energies of the environment. For a thermal environment at all times in equilibrium at inverse temperature β , we thus get $S(M_\tau) - S(M_0) = \beta Q$ where Q is the heat that flowed into the reservoir. On the other hand we can take $\hat{\rho}$ and $\hat{\sigma}$ as equilibrium distributions, say of the weak coupling form

$$\hat{\rho}(M) = \frac{e^{-\beta U(x, \gamma_0)}}{Z_0} h(E)$$

where $M = (x, E)$ combines the micro-state x of the system and the energy E of the environment, $h(E)$ describes the reservoir-distribution, $U(x, \gamma)$ is the energy of the system with parameter γ . Similarly,

$$\hat{\sigma}(M) = \frac{e^{-\beta U(x, \gamma_\tau)}}{Z_\tau} h(E)$$

If we have that $h(E_0) \simeq h(E_\tau)$, i.e., that the energy exchanges to the environment remain small compared to the dispersion of the energy distribution in the reservoir, we get from (27) in that context that

$$\langle e^{-\beta Q - \beta U(x_\tau, \gamma_\tau) + \beta U(x_0, \gamma_0)} \rangle_{\hat{\rho}} = \frac{Z_\tau}{Z_0}$$

which is a version of the Jarzynski relation (22).

Appendix II: Large deviations

For the fluctuation symmetry we are interested in the large deviations of Q_τ/τ from its average as $\tau \uparrow +\infty$. Such deviations can arise from two sources. First there are the large deviations of the work W_τ , which however, we know, satisfies an EFS. Secondly there is the possibility that ΔU also fluctuates to order τ . This second effect is responsible for the deviations from the standard fluctuation relation (2). After all, an energy is typically exponentially distributed and we can thus expect a competition with the fluctuations of the work.

In order to clearly see the influence of the unboundedness of the temporal boundary, we consider here the simplest set-up in which deviations from the standard fluctuation symmetry can be calculated exactly.

We consider a particle moving under the influence of a quadratic potential and a random force. For each time

step $i = 1, 2, \dots, \tau$ we take the work done on the particle y_i to be a random variable distributed according to a Gaussian of average m_i and variance v_i [19]. Let us also consider the analogue of the work (9) as the sum $W_\tau \equiv (y_1 + \dots + y_\tau)$. By construction, the work per unit time $w_\tau \equiv W_\tau/\tau$ is again Gaussian with average $\bar{w}_\tau = (m_1 + \dots + m_\tau)/\tau$ and variance $\sigma_\tau^2 = (v_1 + \dots + v_\tau)/\tau^2$. If $2\bar{w}_\tau = \sigma_\tau^2$, then, automatically, the probability density function $\text{Prob}(W_\tau = w\tau) = \text{Prob}(w_\tau = w)$ satisfies, for all τ ,

$$\frac{\text{Prob}(w_\tau = w)}{\text{Prob}(w_\tau = -w)} = e^w$$

That is the (Gaussian) analogue of the exact fluctuation symmetry (15) for the work (that we here, by the previous construction, assume from the start).

We now consider a new random variable (the analogue of the heat):

$$Q_\tau(w_\tau, y_1, y_\tau) \equiv W_\tau + \eta[(y_\tau - a)^2 - (y_1 - b)^2]$$

where a, b, η are real parameters, with density $\text{Prob}(Q_\tau = q\tau)$. The aim of our toy model is to compute

$$f(q) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \ln \frac{\text{Prob}(Q_\tau = q\tau)}{\text{Prob}(Q_\tau = -q\tau)}$$

That can follow from $f(q) = h(q) - h(-q)$ with $h(q)$ the large deviation rate function of the heat: $\text{Prob}(Q_\tau = q\tau) \simeq \exp(\tau h(q))$. The function $h(q)$ is the Legendre transform of the generating function

$$E(t) = \lim_{\tau} \frac{1}{\tau} \ln E_\tau(t)$$

with

$$E_\tau(t) = \frac{1}{(2\pi)^{\frac{3}{2}} \det^{\frac{1}{2}} C} \int dy e^{tQ_\tau(y)} e^{-\frac{1}{2}(y-\bar{y}) \cdot C^{-1}(y-\bar{y})} \quad (28)$$

where, collectively, $y = (w_\tau, y_1, y_\tau)$ and $\bar{y} \equiv (\bar{w}_\tau, \bar{y}_1, \bar{y}_\tau)$ represent their mean while $C = C_\tau$ corresponds to the covariance matrix of y . Doing the Gaussian integrals in (28) and taking the limit $\tau \rightarrow \infty$ leads to

$$E(t) = \begin{cases} \frac{1}{2}vt^2 + t\bar{w} & \text{if } t \in [-t_*, t_*] \\ +\infty & \text{otherwise} \end{cases}$$

where $t_* = 1/2\eta$, $v = \lim_{\tau} \sigma_\tau^2 = 2\bar{w} = 2 \lim_{\tau} \bar{w}_\tau$.

We are now interested in evaluating the Legendre transform of the above, $h(q) = -\sup_t [qt - E(t)]$. The location of the supremum depends on whether $(q - \bar{w})/v$ lies within or outside the interval $[-t_*, t_*]$. As a result, $h(q)$ becomes a quadratic function within the interval $[-vt_* + \bar{w}, vt_* + \bar{w}]$ and a linear one outside. For the final result for $f(q)$ one distinguishes between the following two cases depending on the value of \bar{w} .

For $vt_\star < \bar{w}$

$$f(q) = \begin{cases} 2qt_\star & \text{for } q \in [0, \bar{w} - vt_\star] \\ -\frac{1}{2v}(q - \bar{w})^2 + qt_\star - \frac{1}{2}vt_\star^2 + \bar{w}t_\star & \text{for } q \in [\bar{w} - vt_\star, \bar{w} + vt_\star] \\ 2\bar{w}t_\star & \text{for } q \in [\bar{w} + vt_\star, \infty) \end{cases} \quad (29)$$

while for $\bar{w} < vt_\star$ one has

$$f(q) = \begin{cases} q & \text{for } q \in [0, -\bar{w} + vt_\star] \\ -\frac{1}{2v}(q - \bar{w})^2 + qt_\star - \frac{1}{2}vt_\star^2 + \bar{w}t_\star & \text{for } q \in [-\bar{w} + vt_\star, \bar{w} + vt_\star] \\ 2\bar{w}t_\star & \text{for } q \in [\bar{w} + vt_\star, \infty) \end{cases} \quad (30)$$

The results of section II C 2 and of [5], i.e. the Gaussian case where $\beta = 1$, are reproduced in (30) by choosing

$\bar{w} = 1$ and $t_\star = 1$ (i.e. $\eta = 1/2$).

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 - [18] This appendix is discussed in a similar form in [17] by one of the authors.
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